Charge density wave and superconducting dome in $TiSe_2$ from electron-phonon interaction.

Matteo Calandra[1] and Francesco Mauri[1]

[1] *CNRS and Institut de Minéralogie et de Physique des Milieux condensés, case 115, 4 place Jussieu, 75252, Paris cedex 05, France*

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At low temperature $TiSe_2$ undergoes a charge density wave instability. Superconductivity is stabilized either by pressure or by Cu intercalation. We show that the pressure phase diagram of $TiSe_2$ is well described by first-principles calculations. At pressures smaller than 4 GPa charge density wave ordering occurs, in agreement with experiments. At larger pressures the disappearing of the charge density wave is due to a stiffening of the short-range force-constants and not to the variation of nesting with pressure. Finally we show that the behavior of T_c as a function of pressure is entirely determined by the electron-phonon interaction without need of invoking excitonic mechanisms. Our work demonstrates that phase-diagrams with competing orders and a superconducting dome are also obtained in the framework of the electron-phonon interaction.

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The interplay between long range charge or magnetic order and superconductivity is one of the highly debated subject in condensed matter-physics. Doping of an antiferromagnetic Mott insulator results in high T_c superconductivity in cuprates[1]. In iron pnictides [2] magnetism plays an important role as the parent compound is often an antiferromagnetic metal with a large magnetic susceptibility [3] and spin fluctuations are believed to survive in the superconducting state [4]. In transition metal dichalcogenides such as 2H-$NbSe_2$ or 2H-$TaSe_2$, multiband superconductivity [5] and charge density wave (CDW) [6] coexist.

Titanium diselenide (1T-$TiSe_2$) belongs to this class of materials, as at $T_{CDW} \approx 200K$ it undergoes a CDW instability characterized by a $2 \times 2 \times 2$ real space superstructure [7]. $TiSe_2$ is not superconducting at low temperature, but CDW is suppressed and superconductivity stabilized either by Cu intercalation (max. $T_c = 4.5$ K) [7] or pressure (max. $T_c = 1.8$ K) [8]. The resulting phase diagram looks similar to that of cuprates with the difference that the spin-density wave order has been replaced by a CDW one[7].

The mechanism at the origin of the CDW and superconducting phases in $TiSe_2$ is currently unknown. The similarity with the phase diagram of other correlated materials and the semimetallic [9] nature of $TiSe_2$ led to the idea [9, 10] that the transition from the high-T semimetallic state to the low-T semimetallic ordered stated is of the Overhauser type[11], namely a Bose-Einstein condensation of excitons driven by correlation effects. Indeed, as proposed in refs. [12, 13], in a semimetal a charge unbalance is poorly screened due to the lack of carriers and the formation of excitons is thus favoured. A Jahn-Teller mechanism has also been proposed[14, 15] to account for CDW in $TiSe_2$ and in dichalcogenides in general [16]. This claim is supported by thermal diffuse scattering data [17] showing the occurrence of a soft-phonon mode at zone boundary. However the origin of the softening is unclear as no first-principles calculations of the $TiSe_2$ phonon dispersion and electron-phonon coupling are available. It is then unknown if density functional theory (DFT) fails in predicting the CDW and superconducting orders.

In this work we demonstrate that the complete $TiSe_2$ pressure phase-diagram is reproduced by first principles calculations. We show that the disappearing of the CDW at finite applied pressure (P) is due to the local chemistry around a Ti atom while the pinning of the CDW is determined by the electron-phonon coupling. Excitonic or nesting effects are not the relevant interactions to describe the $TiSe_2$ pressure phase-diagram.

The DFT band structure [18] and Fermi surfaces of $TiSe_2$ at ambient pressure are shown in Fig. 1. Our results are in agreement with previous works [27, 28]. Four bands cross the Fermi level. A narrow Ti-derived d-band is almost entirely unoccupied except around the L point where it forms elongated and flat hole-pockets (in violet). A Se 4p derived band weakly hybridizes with Ti states and forms an electron-pocket centered at Γ having the form of a small ellipsoid with larger axis parallel to the $k_z = 0$ plane. Finally the other two bands are formed by strongly hybridized Se-p and Ti-d states. Hydrostatic pressure weakly affects the band structure except for an increase of the Se p band bandwidth.

The phonon dispersions [18] at pressure P=0,5 and 10 GPa are shown in Fig. 2. At zero pressure we find that the system is dynamically unstable at the L and M points, consistent with a $2\times2\times1$ (M) or a $2\times2\times2$ (L) real-space superstructure in agreement with diffraction data [7]. As pressure is increased, the CDW disappears at $P \approx 4$ GPa. Transport data [9] support the occurrence of a superconducting state in the region between 2 and 4 GPa. It is unclear if superconductivity coexist or not with CDW order. Given that (i) anharmonic effects (neglected here) should be important close to the transition to the CDW state and should reduce the critical pressure for the occurrence of CDW and (ii) the experimental phase diagram at finite pressure is only based on transport measurements,

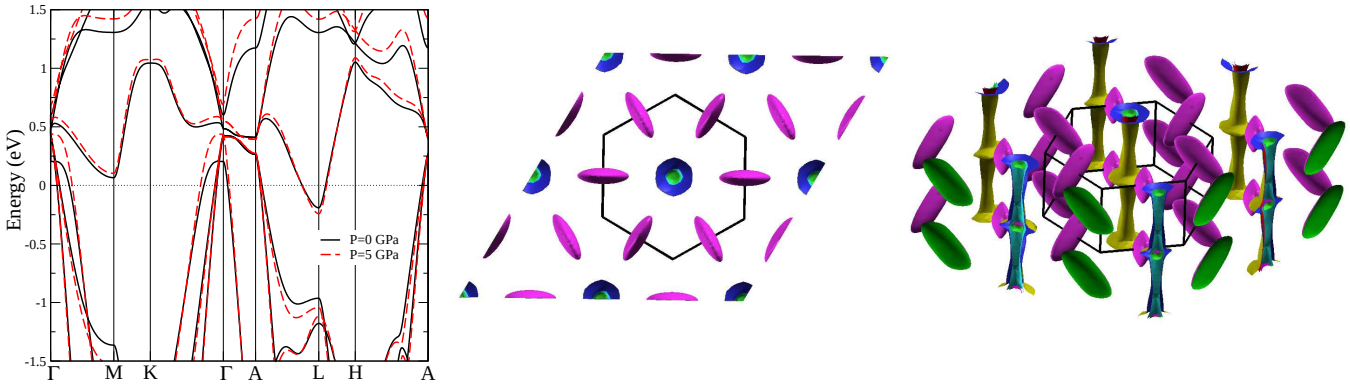

FIG. 1: (color online):(Left) $TiSe_2$ electronic structure at $P = 0$ and 5 GPa and (center and right) $P = 0$ GPa Fermi surface.

our results are in excellent agreement with experimental finding. Thus DFT correctly describes the occurrence of charge density way in $TiSe_2$ at zero and finite pressure.

To address the microscopic mechanism responsible for the occurrence of CDW and its suppression under pressure we calculate the static bare susceptibility $\chi_0(\mathbf{q}) = \frac{2}{N_k}\sum_{\mathbf{k}nm}\frac{f_{\mathbf{k}+\mathbf{q}n}-f_{\mathbf{k}m}}{\epsilon_{\mathbf{k}+\mathbf{q}n}-\epsilon_{\mathbf{k}m}}$ and the nesting factor $N_f(\mathbf{q}) = \frac{2}{N_k}\sum_{\mathbf{k}nm}\delta(\epsilon_{\mathbf{k}+\mathbf{q}n})\delta(\epsilon_{\mathbf{k}m})$, where $\epsilon_{\mathbf{k}m}$ are the DFT-bands measured from the Fermi level. As $\chi_0(\mathbf{q})$ coincides with the electron-phonon contribution to the static phonon self-energy assuming constant matrix elements, it represents the electron-phonon correction to the phonon frequencies squared. A minimum in $\chi_0(\mathbf{q})$ means a softening in $\omega^2_{\mathbf{q}\nu}$. As shown in Fig. 2, $\chi_0(\mathbf{q})$ has a minimum both at M and L and $N_f(\mathbf{q})$ peaks at M and L. However both quantities are essentially unaffected by pressure between 0 and 5 GPa, nesting cannot be responsible for the disappearing of the CDW at 4 GPa.

The mechanism responsible for the disappearance of CDW under pressure can be understood by considering the force constants $C_{IJ}(P)$ at a given pressure P, where I, J label the atoms in the $4\times4\times2$ real-space supercell. A new set of short-range force constants $C^{SR}_{IJ}(P)$ is obtained from $C_{IJ}(P)$ by setting to zero the force constants at distances larger than the Ti-Se bond length. Then we define:

$$\tilde{C}_{IJ}(P) \;=\; C_{IJ}(0) - C^{SR}_{IJ}(0) + C^{SR}_{IJ}(P). \qquad (1)$$

The force-constants $\tilde{C}_{IJ}(P)$ and $C_{IJ}(0)$ only differ by short-range terms as they both include the same long-range behavior calculated at $P = 0$. From $\tilde{C}_{IJ}(P)$ we obtain new phonon frequencies at any phonon-momentum by Fourier interpolation. In Fig. 10 the phonon frequencies obtained with the aforementioned procedure are compared with standard linear-response calculations. As it can be seen the two are very similar and, most important, the CDW disappears simply by removing the short-range force-constants at P=0 and replacing them with that at $P = 10$ GPa. The disappearing of the CDW in $TiSe_2$ is not driven by any electronic mechanism or any long-range interaction but it is due to the stiffening of the nearest-neighbors Ti-Se force-constants under applied pressure. The occurrence of a soft-phonon mode is thus inherent to the local environment around the transition metal atom in the $TiSe_2$ layer.

P(GPa)	λ	$\omega_{\log}$(meV)	T_c(K)
5.0	1.57	7.0	0.84
7.0	0.84	11.0	0.58
10.0	0.62	15.1	0.38

TABLE I: Calculated superconducting properties of $TiSe_2$ using McMillan formula ($\mu^* = 0.1$).

We then consider the superconducting properties of $TiSe_2$ at pressures $P \geq 5$ GPa. We calculate the electron-phonon coupling $\lambda_{\mathbf{q}\nu}$ for a phonon mode ν with momentum $\mathbf{q}$ and phonon frequency $\omega_{\mathbf{q}\nu}$, namely:

$$\lambda_{\mathbf{q}\nu} = \frac{4}{\omega_{\mathbf{q}\nu}N(0)N_k}\sum_{\mathbf{k},n,m}|g^{\nu}_{\mathbf{k}n,\mathbf{k}+\mathbf{q}m}|^2\delta(\epsilon_{\mathbf{k}n})\delta(\epsilon_{\mathbf{k}+\mathbf{q}m}). \qquad (2)$$

The matrix element in Eq. 2 is $g^{\nu}_{\mathbf{k}n,\mathbf{k}+\mathbf{q}m} = \langle\mathbf{k}n|\delta V/\delta u_{\mathbf{q}\nu}|\mathbf{k}+\mathbf{q}m\rangle/\sqrt{2\omega_{\mathbf{q}\nu}}$, where V is the Kohn-Sham potential and $u_{\mathbf{q}\nu}$ is the amplitude of the phonon displacement and $N(0)$ is the density of states at the Fermi level. The critical temperatures obtained with McMillan formula and the parameters in table I are in qualitative agreement with experiments although in experiments superconductivity occurs in a narrower range of pressures. This discrepancy is probably related to the use of a McMillan type of approach to deduce the critical temperature and to the neglect of anharmonic effects.

We calculate the Eliashberg function

$$\alpha^2F(\omega) = \frac{1}{2N_q}\sum_{\mathbf{q}\nu}\lambda_{\mathbf{q}\nu}\omega_{\mathbf{q}\nu}\delta(\omega-\omega_{\mathbf{q}\nu}) \qquad (3)$$

and the integral $\lambda(\omega) = 2\int_0^{\omega}d\omega'\alpha^2F(\omega')/\omega'$. At $P = 5$

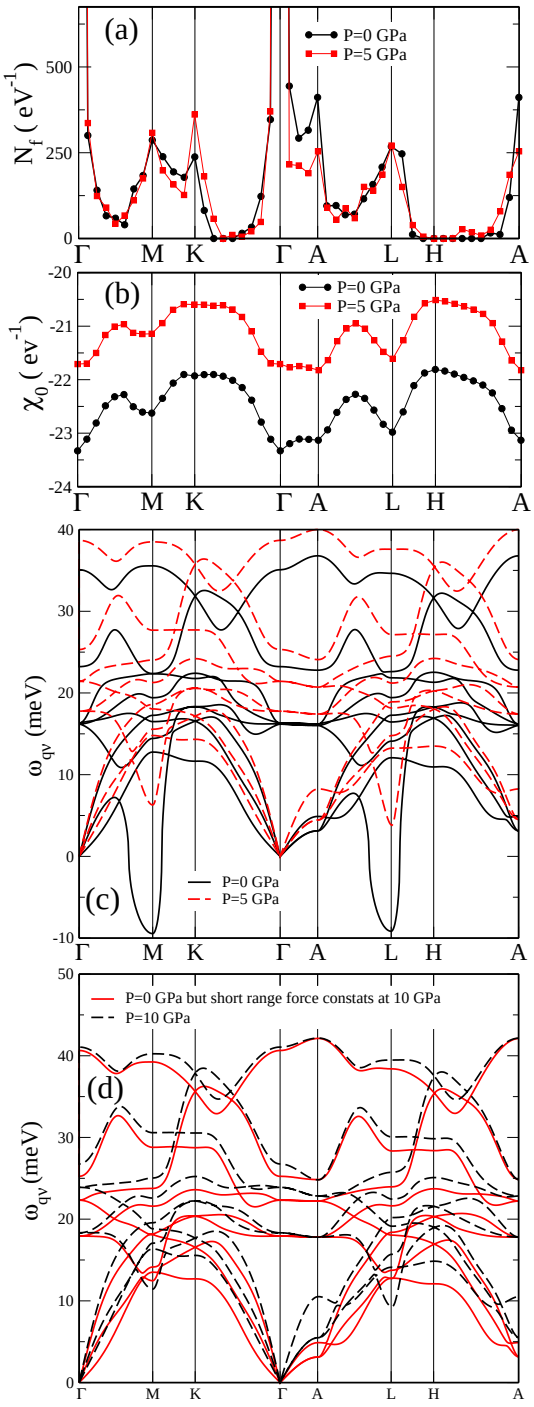

FIG. 2: (color online) $TiSe_2$ (a) Nesting factor, (b) static susceptibility and (c) (d) phonon dispersion as a function hydrostatic pressure. In panel (d) the continuous line phonon dispersion is obtained by replacing the nearest neighbours Ti-Se force constants in the $P = 0$ GPa force constant matrix with those at $P = 10$ GPa.

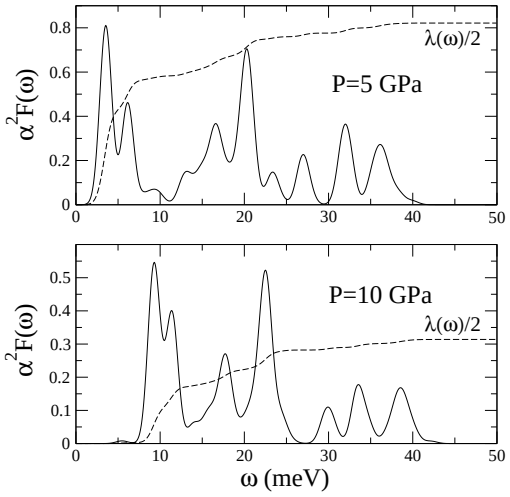

FIG. 3: Eliashberg function and integrated Eliashberg function $\lambda(\omega)$ at 0 and 5 GPa

GPa the Eliashberg function is dominated by the soft mode [29] at low energy that contributes to most of the coupling. As the pressure is raised, the low energy mode hardens (see Fig. 2) and the average electron-phonon coupling is reduced, as shown in Fig. 3.

In the present work we have shown that the finite pressure phase diagram of $TiSe_2$ can be entirely explained by the local chemistry around a Ti atom and by the electron-phonon interaction. In more details, the disappearing of the CDW at finite pressure is determined by the stiffening of the Ti-Se nearest-neighbours short-range force-constants while the static bare electronic susceptibility determines the ordering vector at which the CDW locks-in. The electron-phonon interaction alone does not induce a CDW, as it is clear from the 5 GPa calculation.

In previous works on other transition metal dichalcogenides it was shown that nesting is indeed irrelevant in determining CDW order [30–32] and that DFT is able to reproduce the occurrence of CDW in 2H-$NbSe_2$ [32] and 1T-TaS_2 [33]. In all these works the origin of the CDW was attributed to the electron-phonon interaction. In our work we show that, although electronic susceptibility is relevant in determining the ordering vector, the local chemistry is the real responsible for the occurrence of CDW. More exotic mechanisms such as an Overhauser transition [9] or excitonic phases [10] are unlikely.

Our work reproduces also the main features of the superconducting state of $TiSe_2$ as it explains the dome-like shape of Tc versus pressure found in experiments [8]. Superconductivity is driven by the softening of the phonon mode related to the charge density wave. As the mode is very soft, substantial anharmonic effects are to be expected. The inclusion of these effects would harden the phonon frequency of the soft mode and shift the dome region in which superconductivity takes place to lower pressure in even better agreement with experimental data.

Several authors [7, 8] pointed out the strong similarity of the phase diagram of $TiSe_2$ with cuprates and suggested a non-conventional pairing mechanism for $TiSe_2$. Our work shows that this similarity is only apparent as here superconductivity is phonon-mediated. Furthermore our work demonstrates that exotic phase diagrams including dome-like superconducting regions, as those occurring in Cuprates, Pnictides or Cobaltates can also arise from an electron-phonon mechanism. Thus, the apparent similarity of these phase diagrams to the cuprate case cannot be considered a fingerprint of electronic correlation.

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